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(71)Applicant : MITSUI MINING & SMELTING CO LTD

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(72)Inventor : NUMATA KOICHI
KAGEI SHINYA**(54) POSITIVE ELECTRODE MATERIAL FOR NONAQUEOUS ELECTROLYTE SECONDARY BATTERY, ITS MANUFACTURE AND BATTERY USING THE MATERIAL****(57)Abstract:**

PROBLEM TO BE SOLVED: To provide a positive electrode material for a nonaqueous electrolyte secondary battery with a larger capacity and enhanced cycle property, a manufacturing method thereof and a battery using therewith.

SOLUTION: This positive electrode material for a nonaqueous electrolyte secondary battery is represented by the formula $\text{Li}[\text{Mn}_{2-x-y}\text{Li}_x\text{Me}_y]\text{O}_4$, where $0 < x \leq 0.2$, $0 < y \leq 0.2$, and Me is Al, Co, Cr, Fe, Ni, Mg or Ti. This material is manufactured by mixing the raw materials including the elements other than lithium and then mixing a lithium salt with the mixture.

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|-----------|------------------|----------|---|
| (21) 出願番号 | 特願平9-175127 | (71) 出願人 | 000006183 三井金属鉱業株式会社 東京都中央区日本橋室町2丁目1番1号 |
| (22) 出願日 | 平成9年(1997) 6月17日 | (72) 発明者 | 沼田 幸一 広島県竹原市港町1-8-11 |
| | | (72) 発明者 | 藤井 慎也 広島県竹原市本町2-7-2 304号 |

(54) 【発明の名称】 非水電解液二次電池用正極材料及びその製造方法及びこれを用いた電池

(57) 【要約】

【課題】 高容量でサイクル特性に優れた非水電解液二次電池用正極材料及びその製造方法及びこれを用いた電池を提供する。

【解決手段】 一般式 $\text{Li}[\text{Mn}_{2-x-y}\text{Li}_x\text{Me}_y]\text{O}_4$ ($0 < x \leq 0.2$, $0 < y \leq 0.2$, $\text{Me}: \text{Al}, \text{Co}, \text{Cr}, \text{Fe}, \text{Ni}, \text{Mg}, \text{Ti}$) で表される非水電解液二次電池用正極材料。また、一般式 $\text{Li}[\text{Mn}_{2-x-y}\text{Li}_x\text{Me}_y]\text{O}_4$ ($0 < x \leq 0.2$, $0 < y \leq 0.2$, $\text{Me}: \text{Al}, \text{Co}, \text{Cr}, \text{Fe}, \text{Ni}, \text{Mg}, \text{Ti}$) で表される非水電解液二次電池用正極材料の製造方法であって、まず Li 以外の元素を含む原料を混合し、続いて Li 塩を投入して再度混合することの特徴とする非水電解液二次電池用正極材料の製造方法。また、上記非水電解液二次電池用正極材料を用いた非水電解液二次電池。

【特許請求の範囲】

【請求項1】 一般式 $Li[Mn_{2-x-y}Li_xMe_y]O_4$ ($0 < x \leq 0.2$, $0 < y \leq 0.2$, $Me: Al, Co, Cr, Fe, Ni, Mg, Ti$) で表される非水電解液二次電池用正極材料。

【請求項2】 一般式 $Li[Mn_{2-x-y}Li_xMe_y]O_4$ ($0 < x \leq 0.2$, $0 < y \leq 0.2$, $Me: Al, Co, Cr, Fe, Ni, Mg, Ti$) で表される非水電解液二次電池用正極材料の製造方法であって、まず Li 以外の元素を含む原料を混合し、続いて Li 塩を投入して再度混合することを特徴とする非水電解液二次電池用正極材料の製造方法。

【請求項3】 請求項1記載の非水電解液二次電池用正極材料を用いた非水電解液二次電池。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、リチウム二次電池で代表される、非水電解液二次電池に用いられる正極材料としての $Li-Mn$ 複合酸化物、及びその製造方法及びこれを用いた電池に関するものである。

【0002】

【従来技術】 近年、AV機器あるいはパソコン等の電子機器のポータブル化、コードレス化が急速に進んでおり、これらの駆動用電源として小型、軽量で高エネルギー密度を有する二次電池への要求が高い。このような要求に対し、非水系二次電池、特にリチウム二次電池は、とりわけ高電圧、高エネルギー密度を有する電池としての期待が大きい。これらの要求を満たすリチウム二次電池用の正極材料としてリチウムをインターカレーション、デインターカレーションすることのできる $LiCoO_2$ 、 $LiNiO_2$ あるいはこれらの酸化物に遷移金属元素を一部置換した複合酸化物などの層状化合物の研究開発が盛んに行われている。

【0003】 また、層状構造を持たないが、 $LiCoO_2$ 等と同様の4V級の高電圧を有する安価な材料として、 $Li-Mn$ 複合酸化物である $LiMn_2O_4$ が、また電圧は約3Vと若干低い $LiMnO_2$ の開発も進められている。しかし、これら $Li-Mn$ 複合酸化物をリチウム二次電池用の正極材料として用いた場合、従来の $LiCoO_2$ や $LiNiO_2$ を正極材料として用いた場合に比較してサイクル特性に劣るという問題があった。この対策として、 Mn の一部を Li で置換したり、 Al で置換するという方法も試みたが、ある程度の改善は得られるものの充分ではない。また、電池容量も小さいという問題があった。

【0004】

【発明が解決しようとする課題】 本発明は、高容量でサイクル特性に優れた非水電解液二次電池用正極材料及びその製造法及びこれを用いた電池を提供することを目的とする。

【0005】

【課題を解決するための手段】 よって、本発明は、一般式 $Li[Mn_{2-x-y}Li_xMe_y]O_4$ ($0 < x \leq 0.2$, $0 < y \leq 0.2$, $Me: Al, Co, Cr, Fe, Ni, Mg, Ti$) で表される非水電解液二次電池用正極材料である。また、本発明は、一般式 $Li[Mn_{2-x-y}Li_xMe_y]O_4$ ($0 < x \leq 0.2$, $0 < y \leq 0.2$, $Me: Al, Co, Cr, Fe, Ni, Mg, Ti$) で表される非水電解液二次電池用正極材料の製造方法であって、まず Li 以外の元素を含む原料を混合し、続いて Li 塩を投入して再度混合することを特徴とする非水電解液二次電池用正極材料の製造方法である。また、本発明は、上記非水電解液二次電池用正極材料を用いた非水電解液二次電池である。

【0006】 x 値が0.2以上では、初期容量の低下が大きく、また y 値が0.2以上でも同様に初期容量の低下が大きい。

【0007】

【実施例】 以下、実施例、比較例に基づいて本発明を具体的に説明する。なお、本発明は以下に示す原料、電池構成等に限定されるものではない。

【0008】 実施例1

電解二酸化マンガンと、水酸化アルミニウムを $Mn: Al = 1.85: 0.05$ となるように混合し、続いて、炭酸リチウムを、 $Li: Mn = 1.1: 1.85$ となるように秤量し、ボールミルで混合後、電気炉中で $800^\circ C$ で20時間焼成し、解砕して $Li-Mn$ 複合酸化物を生成した。この $Li-Mn$ 複合酸化物を正極材料としてコイン電池を作製し、放電試験を行い、初期容量及びサイクル特性を測定し、その結果を表1に示す。なお、コイン電池の正極合剤として、この $Li-Mn$ 複合酸化物85重量部に対して、アセチレンブラック10重量部およびフッ素樹脂系結着剤5重量部の割合で混合したものを加重3tで加圧成型してペレットとしたものを用いた。電解液としてはプロピレンカーボネートと1,2-ジメトキシエタンの1:1の混合溶媒中に1モル/lになるようテトラフルオロホウ酸リチウム ($LiBF_4$) を溶解したのを用い、セパレーターに含ませて使用した。負極材としては金属リチウムを用いた。

【0009】

【表1】

表1. 電池特性評価結果

| | 合金組成 | 初期容量 mAh/g | 50サイクル時 容量維持率(%) |
|------|---------------------------|---------------|---------------------|
| 実施例1 | LiMn1.85Li0.1 Al0.05O4 | 115 | 95.2 |
| 実施例2 | LiMn1.85Li0.1 Co0.05O4 | 118 | 94.6 |
| 実施例3 | LiMn1.85Li0.1 Cr0.05O4 | 117 | 94.0 |
| 実施例4 | LiMn1.85Li0.1 Fe0.05O4 | 116 | 94.2 |
| 実施例5 | LiMn1.85Li0.1 Ni0.05O4 | 112 | 95.5 |
| 実施例6 | LiMn1.85Li0.1 Mg0.05O4 | 120 | 93.8 |
| 実施例7 | LiMn1.85Li0.1 Ti0.05O4 | 117 | 93.8 |
| 比較例1 | LiMn2O4 | 125 | 87.0 |
| 比較例2 | LiMn1.85 Al0.15O4 | 102 | 95.0 |
| 比較例3 | LiMn1.85 Li0.15O4 | 107 | 90.0 |
| 比較例4 | LiMn1.85Li0.1 Al0.05O4 | 112 | 93.5 |

【0010】実施例2～7

電解二酸化マンガンを、Me:Co, Cr, Fe, Ni, Mg, Tiの各水酸化物をMn:Me=1.85:0.05となるように混合し、続いて、炭酸リチウムを、Li:Mn=1.1:1.85となるように秤量し、ボールミルで混合後、電気炉中で800℃で20時間焼成し、解砕してLi-Mn複合酸化物を生成した。このLi-Mn複合酸化物を正極活物質として、実施例1と同様にして、コイン電池を作製し、放電試験を行い、初期容量及びサイクル特性を測定し、その結果を表1に示す。

【0011】比較例1

電解二酸化マンガンを、炭酸リチウムを原料として、Li:Mn=1.1:2となるように秤量し、ボールミルで混合後、電気炉中で800℃で20時間焼成し、解砕してLi-Mn複合酸化物を生成した。このLi-Mn複合酸化物を正極活物質とし、実施例1と同様にして、コイン電池を作製し、放電試験を行い、初期容量及びサイクル特性を測定し、その結果を表1に示す。

【0012】比較例2

電解二酸化マンガンを、水酸化アルミニウムを、Mn:Al=1.85:0.15となるように混合し、続いて、炭酸リチウムを、Li:Mn=1.1:1.85となるように秤量し、ボールミルで混合後、電気炉中で800℃で20時間焼成し、解砕してLi-Mn複合酸化物を生成した。このLi-Mn複合酸化物を正極活物質

とし、実施例1と同様にして、コイン電池を作製し、放電試験を行い、初期容量及びサイクル特性を測定し、その結果を表1に示す。

【0013】比較例3

電解二酸化マンガンを、炭酸リチウムを、Li:Mn=1.15:1.85となるように秤量し、ボールミルで混合後、電気炉中で800℃で20時間焼成し、解砕してLi-Mn複合酸化物を生成した。このLi-Mn複合酸化物を正極活物質とし、実施例1と同様にして、コイン電池を作製し、放電試験を行い、初期容量及びサイクル特性を測定し、その結果を表1に示す。

【0014】比較例4

電解二酸化マンガンを、水酸化アルミニウムと、炭酸リチウムを、Li:Al:Mn=1.1:0.05:1.85となるように秤量し、ボールミルで混合後、電気炉中で800℃で20時間焼成し、解砕してLi-Mn複合酸化物を生成した。このLi-Mn複合酸化物を正極活物質とし、実施例1と同様にして、コイン電池を作製し、放電試験を行い、初期容量及びサイクル特性を測定し、その結果を表1に示す。

【0015】

【発明の効果】以上説明したように、本発明によれば、高容量でサイクル特性に優れた非水電解液二次電池用正極材料及びその製造法及びこれを用いた電池を提供することができる。

JAPANESE

[JP,11-007956,A]

AD

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION
TECHNICAL PROBLEM MEANS EXAMPLE

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CLAIMS

[Claim(s)]

[Claim 1] General formula $\text{Li} [\text{Mn}_{2-x-y} \text{Li}_x \text{Me}_y]$ Positive-electrode material for nonaqueous electrolyte rechargeable batteries expressed with O4 ($0 < x \leq 0.2$, $0 < y \leq 0.2$, Me: aluminum, Co, Cr, Fe, nickel, Mg, Ti).

[Claim 2] General formula $\text{Li} [\text{Mn}_{2-x-y} \text{Li}_x \text{Me}_y]$ The manufacture method of the positive-electrode material for nonaqueous electrolyte rechargeable batteries characterized by being the manufacture method of the positive-electrode material for nonaqueous electrolyte rechargeable batteries expressed with O4 ($0 < x \leq 0.2$, $0 < y \leq 0.2$, Me: aluminum, Co, Cr, Fe, nickel, Mg, Ti), mixing the raw material which contains elements other than Li first, throwing in Li salt continuously, and mixing again.

[Claim 3] The nonaqueous electrolyte rechargeable battery using a positive-electrode material for nonaqueous electrolyte rechargeable batteries according to claim 1.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the Li-Mn multiple oxide as a positive-electrode material used for the nonaqueous electrolyte rechargeable battery represented with a lithium secondary battery, its manufacture method, and the cell using this.

[0002]

[Description of the Prior Art] In recent years, portable-izing of electronic equipment, such as an AV equipment or a personal computer, and cordless-ization are progressing quickly, and small and the demand to the rechargeable battery which is lightweight and has high-energy density are high as these power supplies for a drive. The expectation as a cell whose non-drainage system rechargeable battery, especially lithium secondary battery especially have a high voltage and high-energy density to such a demand is great. They are an intercalation, LiCoO₂ which can carry out a day intercalation, and LiNiO₂ about a lithium as a positive-electrode material for lithium secondary batteries which fills these demands. Or research and development of stratified compounds, such as a multiple oxide which replaced a part of transition-metals element by these oxides, are done briskly.

[0003] moreover -- although it does not have the layer structure -- LiCoO₂ etc. -- LiMn₂O₄ which is a Li-Mn multiple oxide as a cheap material which has the 4V class same high voltage -- moreover, voltage -- about 3 -- V and LiMnO₂ low a little Development is also furthered. However, when these Li-Mn multiple oxide is used as a positive-electrode material for lithium secondary batteries, it is conventional LiCoO₂. LiNiO₂ There was a problem that it was inferior to a cycle property as compared with the case where it uses as a positive-electrode material. Although the method of replacing a part of Mn by Li, or replacing it with aluminum as this cure was also tried, although a certain amount of improvement is obtained, it is not enough. Moreover, there was a problem that cell capacity was also small.

[0004]

[Problem(s) to be Solved by the Invention] this invention aims at offering the positive-electrode material for nonaqueous electrolyte rechargeable batteries which was excellent in the cycle property with high capacity, its manufacturing method, and the cell using this.

[0005]

[Means for Solving the Problem] Therefore, this invention is a positive-electrode material for nonaqueous electrolyte rechargeable batteries expressed with general formula Li[Mn_{2-x-y}Li_xMe_y]O₄ (0<x≤0.2, 0<y≤0.2, Me:aluminum, Co, Cr, Fe, nickel, Mg, Ti). Moreover, this invention is at general formula Li[Mn_{2-x-y}Li_xMe_y]O₄ (0<x≤0.2, 0<y≤0.2, Me:aluminum, Co, Cr, Fe, nickel, Mg, Ti). It is the manufacture method of the positive-electrode material for nonaqueous electrolyte rechargeable batteries expressed. It is the manufacture method of the positive-electrode material for nonaqueous electrolyte rechargeable batteries characterized by mixing the raw material which contains elements other than Li first, throwing in Li salt continuously, and mixing again. Moreover, this invention is the nonaqueous electrolyte rechargeable battery which used the above-mentioned positive-electrode material for nonaqueous electrolyte rechargeable batteries.

[0006] The fall of initial capacity has x large values at 0.2 or more, and 0.2 or more have [y value] the large fall of initial capacity similarly.

[0007]

[Example] Hereafter, based on an example and the example of comparison, this invention is explained concretely. In addition, this invention is not limited to a raw material, cell composition, etc. which are shown below.

[0008] By mixing an aluminum hydroxide with example 1 electrolytic manganese dioxide so that it may be set to Mn:aluminum=1.85:0.05, weighing capacity of the lithium carbonate was carried out so that it might be set to Li:Mn=1.1:1.85, and it calcinated after mixture with the ball mill, calcinated at 800 degrees C in the electric furnace for 20 hours, it cracked, and the Li-Mn multiple oxide was generated. A coin cell is produced by making this Li-Mn multiple oxide into positive-electrode material, a spark test is performed, initial capacity and a cycle property are

measured, and the result is shown in Table 1. in addition, the positive electrode of a coin cell -- what carried out pressurization molding of what the acetylene black 10 weight section and the fluororesin system binder 5 weight section came out of comparatively, and was mixed by 3t of loads, and was made into the pellet to this Li-Mn multiple-oxide 85 weight section as a mixture was used It was used using what dissolved the tetrapod fluoroboric-acid lithium (LiBF₄) so that it might be set to one mol -/l into propylene carbonate and the mixed solvent of 1 and 1:1 of 2-dimethoxyethane as the electrolytic solution, having made it contain in a separator. The metal lithium was used as negative-electrode material.

[0009]

[Table 1]

表 1. 電池特性評価結果

| | 合金組成 | 初期容量 mAh/g | 50 サイクル時 容量維持率 (%) |
|-------|---------------------------|---------------|-----------------------|
| 実施例 1 | LiMn1.85Li0.1 Al0.05O4 | 115 | 95.2 |
| 実施例 2 | LiMn1.85Li0.1 Co0.05O4 | 118 | 94.6 |
| 実施例 3 | LiMn1.85Li0.1 Cr0.05O4 | 117 | 94.0 |
| 実施例 4 | LiMn1.85Li0.1 Fe0.05O4 | 116 | 94.2 |
| 実施例 5 | LiMn1.85Li0.1 Ni0.05O4 | 112 | 95.5 |
| 実施例 6 | LiMn1.85Li0.1 Mg0.05O4 | 120 | 93.8 |
| 実施例 7 | LiMn1.85Li0.1 Ti0.05O4 | 117 | 93.8 |
| 比較例 1 | LiMn2O4 | 125 | 87.0 |
| 比較例 2 | LiMn1.85 Al0.15O4 | 102 | 95.0 |
| 比較例 3 | LiMn1.85 Li0.15O4 | 107 | 90.0 |
| 比較例 4 | LiMn1.85Li0.1 Al0.05O4 | 112 | 93.5 |

[0010] By mixing each hydroxide of Me:Co, and Cr, Fe, nickel, Mg and Ti with an example 2 - 7 electrolytic manganese dioxides so that it may be set to Mn:Me=1.85:0.05, weighing capacity of the lithium carbonate was carried out so that it might be set to Li:Mn=1.1:1.85, and it calcinated after mixture with the ball mill, calcinated at 800 degrees C in the electric furnace for 20 hours, it cracked, and the Li-Mn multiple oxide was generated. By making this Li-Mn multiple oxide into a positive active material, like an example 1, a coin cell is produced, a spark test is performed, initial capacity and a cycle property are measured, and the result is shown in Table 1.

[0011] By using a lithium carbonate as a raw material, weighing capacity was carried out to the example of comparison 1 electrolytic manganese dioxide so that it might be set to Li:Mn=1.1:2, and it calcinated after mixture with the ball mill, calcinated at 800 degrees C in the electric furnace for 20 hours, it cracked, and the Li-Mn multiple oxide was generated. This Li-Mn multiple oxide is made into a positive active material, like an example 1, a coin cell is produced, a spark test is performed, initial capacity and a cycle property are measured, and the result is shown in Table 1.

[0012] By mixing an aluminum hydroxide with example of comparison 2 electrolytic manganese dioxide so that it may be set to Mn:aluminum=1.85:0.15, weighing capacity of the lithium carbonate was carried out so that it might be set to Li:Mn=1.1:1.85, and it calcinated after mixture with the ball mill, calcinated at 800 degrees C in the electric furnace for 20 hours, it cracked, and the Li-Mn multiple oxide was generated. This Li-Mn multiple oxide is made into a positive active material, like an example 1, a coin cell is produced, a spark test is performed, initial capacity and a cycle property are measured, and the result is shown in Table 1.

[0013] Weighing capacity of the lithium carbonate was carried out to the example of comparison 3 electrolytic manganese dioxide so that it might be set to Li:Mn=1.15:1.85, and it calcinated after mixture with the ball mill, calcinated at 800 degrees C in the electric furnace for 20 hours, it cracked, and the Li-Mn multiple oxide was

generated. This Li-Mn multiple oxide is made into a positive active material, like an example 1, a coin cell is produced, a spark test is performed, initial capacity and a cycle property are measured, and the result is shown in Table 1.

[0014] Weighing capacity of the lithium carbonate was carried out to the example of comparison 4 electrolytic manganese dioxide, and the aluminum hydroxide so that it might be set to Li:aluminum:Mn=1.1:0.05:1.85, and it calcinated after mixture with the ball mill, calcinated at 800 degrees C in the electric furnace for 20 hours, it cracked, and the Li-Mn multiple oxide was generated. This Li-Mn multiple oxide is made into a positive active material, like an example 1, a coin cell is produced, a spark test is performed, initial capacity and a cycle property are measured, and the result is shown in Table 1.

[0015]
[Effect of the Invention] As explained above, according to this invention, the positive-electrode material for nonaqueous electrolyte rechargeable batteries which was excellent in the cycle property with high capacity, its manufacturing method, and the cell using this can be offered.

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TECHNICAL FIELD

[Industrial Application] this invention relates to the Li-Mn multiple oxide as a positive-electrode material used for the nonaqueous electrolyte rechargeable battery represented with a lithium secondary battery, its manufacture method, and the cell using this.

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PRIOR ART

[Description of the Prior Art] In recent years, portable-izing of electronic equipment, such as an AV equipment or a personal computer, and cordless-ization are progressing quickly, and small and the demand to the rechargeable battery which is lightweight and has high-energy density are high as these power supplies for a drive. The expectation as a cell whose non-drainage system rechargeable battery, especially lithium secondary battery especially have a high voltage and high-energy density to such a demand is great. They are an intercalation, LiCoO₂ which can carry out a day intercalation, and LiNiO₂ about a lithium as a positive-electrode material for lithium secondary batteries which fills these demands. Or research and development of stratified compounds, such as a multiple oxide which replaced a part of transition-metals element by these oxides, are done briskly.

[0003] moreover -- although it does not have the layer structure -- LiCoO₂ etc. -- LiMn₂O₄ which is a Li-Mn multiple oxide as a cheap material which has the 4V class same high voltage -- moreover, voltage -- about 3 -- some [V and] -- low LiMnO₂ Development is also furthered. However, when these Li-Mn multiple oxide is used as a positive-electrode material for lithium secondary batteries, it is conventional LiCoO₂. LiNiO₂ There was a problem that it was inferior to a cycle property as compared with the case where it uses as a positive-electrode material. Although the method of replacing a part of Mn by Li, or replacing it with aluminum as this cure was also tried, although a certain amount of improvement is obtained, it is not enough. Moreover, there was a problem that cell capacity was also small.

[0004]

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EFFECT OF THE INVENTION

[Effect of the Invention] As explained above, according to this invention, the positive-electrode material for nonaqueous electrolyte rechargeable batteries which was excellent in the cycle property with high capacity, its manufacturing method, and the cell using this can be offered.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] this invention aims at offering the positive-electrode material for nonaqueous electrolyte rechargeable batteries which was excellent in the cycle property with high capacity, its manufacturing method, and the cell using this.

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MEANS

[Means for Solving the Problem] Therefore, this invention is a positive-electrode material for nonaqueous electrolyte rechargeable batteries expressed with general formula $\text{Li}[\text{Mn}_{2-x-y}\text{Li}_x\text{Me}_y]\text{O}_4$ ($0 < x \leq 0.2$, $0 < y \leq 0.2$, Me:aluminum, Co, Cr, Fe, nickel, Mg, Ti). Moreover, this invention is at general formula $\text{Li}[\text{Mn}_{2-x-y}\text{Li}_x\text{Me}_y]\text{O}_4$ ($0 < x \leq 0.2$, $0 < y \leq 0.2$, Me:aluminum, Co, Cr, Fe, nickel, Mg, Ti). It is the manufacture method of the positive-electrode material for nonaqueous electrolyte rechargeable batteries expressed. It is the manufacture method of the positive-electrode material for nonaqueous electrolyte rechargeable batteries characterized by mixing the raw material which contains elements other than Li first, throwing in Li salt continuously, and mixing again. Moreover, this invention is the nonaqueous electrolyte rechargeable battery which used the above-mentioned positive-electrode material for nonaqueous electrolyte rechargeable batteries.

[0006] The fall of initial capacity has x large values at 0.2 or more, and 0.2 or more have [y value] the large fall of initial capacity similarly.

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EXAMPLE

[Example] Hereafter, based on an example and the example of comparison, this invention is explained concretely. In addition, this invention is not limited to a raw material, cell composition, etc. which are shown below.

[0008] By mixing an aluminum hydroxide with example 1 electrolytic manganese dioxide so that it may be set to Mn:aluminum=1.85:0.05, weighing capacity of the lithium carbonate was carried out so that it might be set to Li:Mn=1.1:1.85, and it calcinated after mixture with the ball mill, calcinated at 800 degrees C in the electric furnace for 20 hours, it cracked, and the Li-Mn multiple oxide was generated. A coin cell is produced by making this Li-Mn multiple oxide into positive-electrode material, a spark test is performed, initial capacity and a cycle property are measured, and the result is shown in Table 1. in addition, the positive electrode of a coin cell -- what carried out pressurization molding of what the acetylene black 10 weight section and the fluororesin system binder 5 weight section came out of comparatively, and was mixed by 3t of loads, and was made into the pellet to this Li-Mn multiple-oxide 85 weight section as a mixture was used. It was used using what dissolved the tetrapod fluoroboric-acid lithium (LiBF₄) so that it might be set to one mol -/l into propylene carbonate and the mixed solvent of 1 and 1:1 of 2-dimethoxyethane as the electrolytic solution, having made it contain in a separator. The metal lithium was used as negative-electrode material.

[0009]

[Table 1]

表 1. 電池特性評価結果

| | 合金組成 | 初期容量 mAh/g | 50サイクル時 容量維持率(%) |
|-------|------------------------------------|---------------|---------------------|
| 実施例 1 | Li Mn 1.85 L i 0.1 A l 0.05 O 4 | 1 1 5 | 9 5 . 2 |
| 実施例 2 | Li Mn 1.85 L i 0.1 C o 0.05 O 4 | 1 1 8 | 9 4 . 6 |
| 実施例 3 | Li Mn 1.85 L i 0.1 C r 0.05 O 4 | 1 1 7 | 9 4 . 0 |
| 実施例 4 | Li Mn 1.85 L i 0.1 F e 0.05 O 4 | 1 1 6 | 9 4 . 2 |
| 実施例 5 | Li Mn 1.85 L i 0.1 N i 0.05 O 4 | 1 1 2 | 9 5 . 5 |
| 実施例 6 | Li Mn 1.85 L i 0.1 M g 0.05 O 4 | 1 2 0 | 9 3 . 8 |
| 実施例 7 | Li Mn 1.85 L i 0.1 T i 0.05 O 4 | 1 1 7 | 9 3 . 8 |
| 比較例 1 | Li Mn 2 O 4 | 1 2 5 | 8 7 . 0 |
| 比較例 2 | Li Mn 1.85 A l 0.15 O 4 | 1 0 2 | 9 5 . 0 |
| 比較例 3 | Li Mn 1.85 L i 0.15 O 4 | 1 0 7 | 9 0 . 0 |
| 比較例 4 | Li Mn 1.85 L i 0.1 A l 0.05 O 4 | 1 1 2 | 9 3 . 5 |

[0010] By mixing each hydroxide of Me:Co, and Cr, Fe, nickel, Mg and Ti with an example 2 - 7 electrolytic manganese dioxides so that it may be set to Mn:Me=1.85:0.05, weighing capacity of the lithium carbonate was carried out so that it might be set to Li:Mn=1.1:1.85, and it calcinated after mixture with the ball mill, calcinated at

800 degrees C in the electric furnace for 20 hours, it cracked, and the Li-Mn multiple oxide was generated. By making this Li-Mn multiple oxide into a positive active material, like an example 1, a coin cell is produced, a spark test is performed, initial capacity and a cycle property are measured, and the result is shown in Table 1.

[0011] By using a lithium carbonate as a raw material, weighing capacity was carried out to the example of comparison 1 electrolytic manganese dioxide so that it might be set to $\text{Li:Mn}=1.1:2$, and it calcinated after mixture with the ball mill, calcinated at 800 degrees C in the electric furnace for 20 hours, it cracked, and the Li-Mn multiple oxide was generated. This Li-Mn multiple oxide is made into a positive active material, like an example 1, a coin cell is produced, a spark test is performed, initial capacity and a cycle property are measured, and the result is shown in Table 1.

[0012] By mixing an aluminum hydroxide with example of comparison 2 electrolytic manganese dioxide so that it may be set to $\text{Mn:aluminum}=1.85:0.15$, weighing capacity of the lithium carbonate was carried out so that it might be set to $\text{Li:Mn}=1.1:1.85$, and it calcinated after mixture with the ball mill, calcinated at 800 degrees C in the electric furnace for 20 hours, it cracked, and the Li-Mn multiple oxide was generated. This Li-Mn multiple oxide is made into a positive active material, like an example 1, a coin cell is produced, a spark test is performed, initial capacity and a cycle property are measured, and the result is shown in Table 1.

[0013] Weighing capacity of the lithium carbonate was carried out to the example of comparison 3 electrolytic manganese dioxide so that it might be set to $\text{Li:Mn}=1.15:1.85$, and it calcinated after mixture with the ball mill, calcinated at 800 degrees C in the electric furnace for 20 hours, it cracked, and the Li-Mn multiple oxide was generated. This Li-Mn multiple oxide is made into a positive active material, like an example 1, a coin cell is produced, a spark test is performed, initial capacity and a cycle property are measured, and the result is shown in Table 1.

[0014] Weighing capacity of the lithium carbonate was carried out to the example of comparison 4 electrolytic manganese dioxide, and the aluminum hydroxide so that it might be set to $\text{Li:aluminum:Mn}=1.1:0.05:1.85$, and it calcinated after mixture with the ball mill, calcinated at 800 degrees C in the electric furnace for 20 hours, it cracked, and the Li-Mn multiple oxide was generated. This Li-Mn multiple oxide is made into a positive active material, like an example 1, a coin cell is produced, a spark test is performed, initial capacity and a cycle property are measured, and the result is shown in Table 1.

[Translation done.]